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Dissipative Particle Dynamics at Isothermal, Isobaric Conditions Using Shardlow-Like Splitting Algorithms

by John K. Brennan and Martin Lísal

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14. ABSTRACT
A numerical integration scheme based upon the Shardlow-splitting algorithm is presented for the constant-temperature, constant-pressure Dissipative Particle Dynamics (DPD-P) method, where both a deterministic (Hoover) and stochastic (Langevin) barostat are considered under both uniform and nonuniform dilation. The approaches are verified using both a standard DPD fluid model and a coarse-grain solid model. For completeness, the Fokker-Planck equation and derivation of the fluctuation-dissipation theorem are included.

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1. Introduction

Extensions of the original constant-temperature Dissipative Particle Dynamics (DPD) method (*1*, *2*) have been developed, including methods that impose constant-pressure (DPD-P) (*3*, *4*) conditions. Formulated from an extended system, the DPD-P method can be implemented using either a Hoover or Langevin barostat (*3*). DPD-P allows control over both the temperature and the pressure, where in typical fashion the cell volume fluctuates to satisfy the imposed pressure.

When applying any DPD method, numerical integration of the equations-of-motion (EOM) is a key consideration since the stochastic component requires special attention. Efficient and accurate integration schemes are required to maintain reasonable time step sizes, thus allowing for the simulation of actual mesoscale events. Moreover, the integration is a nontrivial task due to the pairwise coupling of particles through the random and dissipative forces (*5*). In recent work (*6*), a comprehensive description of numerical integration schemes based upon the Shardlow-splitting algorithm (SSA) was presented for the constant-temperature DPD method. The original SSA formulated for systems of equal-mass particles was extended to systems of unequal-mass particles. Both a velocity-Verlet scheme and an implicit scheme were formulated for the integration of the fluctuation-dissipation contribution where the velocity-Verlet scheme consistently performed better.

In this work, we formulate the SSA for the DPD-P method, where we verify the method using both the standard DPD fluid (pure and binary mixtures) (*7*) and a coarse-grain solid model (*8*). For completeness, derivations of the Fokker-Planck equation (FPE) and the fluctuation-dissipation theorem (FDT) are included.

2. Formulations of DPD at Fixed Temperature and Pressure Using Shardlow-Like Splitting Numerical Discretization

2.1 General Formulation of DPD

DPD particles are defined by a mass m_i, position $\mathbf{r}_i$, and momentum $\mathbf{p}_i$. The particles interact with each other via a pairwise force $\mathbf{F}_{ij}$ that is written as the sum of a conservative force $\mathbf{F}_{ij}^C$, dissipative force $\mathbf{F}_{ij}^D$, and random force $\mathbf{F}_{ij}^R$:

$$\mathbf{F}_{ij} = \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R . \tag{1}$$

$\mathbf{F}_{ij}^C$ is given as the negative derivative of a coarse-grain potential, u_{ij}^{CG}, expressed as

$$\mathbf{F}_{ij}^{C} = -\frac{\mathrm{d}u_{ij}^{CG}}{\mathrm{d}r_{ij}}\frac{\mathbf{r}_{ij}}{r_{ij}}, \tag{2}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the separation vector between particle i and particle j and $r_{ij} = \left|\mathbf{r}_{ij}\right|$. The remaining two forces, $\mathbf{F}_{ij}^{D}$ and $\mathbf{F}_{ij}^{R}$, can be interpreted as a means to compensate for the degrees-of-freedom neglected by coarse-graining. The conservative force is not specified by the DPD formulation and can be chosen to include any forces that are appropriate for a given application, including multibody interactions (e.g., [*8–10*]). $\mathbf{F}_{ij}^{D}$ and $\mathbf{F}_{ij}^{R}$ are defined as

$$\mathbf{F}_{ij}^{D} = -\gamma_{ij}\omega^{D}\left(r_{ij}\right)\left(\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\right)\frac{\mathbf{r}_{ij}}{r_{ij}} \tag{3}$$

and

$$\mathbf{F}_{ij}^{R} = \sigma_{ij}\omega^{R}\left(r_{ij}\right)W_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\ , \tag{4}$$

where γ_{ij} and σ_{ij} are the friction coefficient and noise amplitude between particle i and particle j, respectively, $\mathbf{v}_{ij} = \frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}$, and W_{ij} are independent Wiener processes such that $W_{ij} = W_{ji}$. The weight functions $\omega^{D}\left(r\right)$ and $\omega^{R}\left(r\right)$ vanish for $r \geq r_c$ where r_c is the cut-off radius.

Note that $\mathbf{F}_{ij}^{C}$ is completely independent of $\mathbf{F}_{ij}^{D}$ and $\mathbf{F}_{ij}^{R}$, while $\mathbf{F}_{ij}^{D}$ and $\mathbf{F}_{ij}^{R}$ are not independent but rather coupled through a fluctuation-dissipation relation. This coupling arises from the requirement that in the thermodynamic limit, the system samples the corresponding probability distribution.

2.2 Constant-Pressure DPD

Generally, a barostat in an extended system approach is introduced via variables ε, p_ε, and W_ε. ε is defined as the logarithm of the system volume V, $\varepsilon = \ln\frac{V}{V(0)}$ where $V(0)$ is the volume at $t = 0$, W_ε is a mass parameter associated with ε, and p_ε is the momentum conjugate to ε (*11*). A Langevin barostat can be incorporated into this extended system approach via additional dissipative and random terms (*12*). The DPD-P method, first introduced by Jakobsen (*3*), was formulated for both a Hoover and Langevin barostat, where soon after Trofimov et al. presented a similar formulation based upon an Andersen barostat (*4*). For uniform dilation using a Langevin barostat, the EOM are given as

$$
\begin{aligned}
\mathrm{d}\mathbf{r}_i &= \frac{\mathbf{p}_i}{m_i}\mathrm{d}t + \frac{p_\varepsilon}{W_\varepsilon}\mathbf{r}_i\mathrm{d}t \\
\mathrm{d}\mathbf{p}_i &= \sum_{j\neq i}\left(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R\right)\mathrm{d}t - \left(1+\frac{d}{N_f}\right)\frac{p_\varepsilon}{W_\varepsilon}\mathbf{p}_i\mathrm{d}t \qquad \left(i=1,\ldots,N\right) \\
\mathrm{d}\ln V &= \frac{dp_\varepsilon}{W_\varepsilon}\mathrm{d}t \\
\mathrm{d}p_\varepsilon &= F_\varepsilon \mathrm{d}t
\end{aligned}
\quad , \tag{5}
$$

where $F_\varepsilon = dV\left(P-P_0\right)+\frac{d}{N_f}\sum_i \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{m_i} - \gamma_P p_\varepsilon + \sigma_P W_p$, $P=\frac{1}{dV}\left(\sum_i \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{m_i}+\sum_i\sum_{j>i}\mathbf{F}_{ij}^C\cdot\mathbf{r}_{ij}\right)$ is the instantaneous pressure, P_0 is the imposed pressure, d is the dimensionality of the system, $N_f = dN - d$, γ_P and σ_P are the Langevin barostat parameters, and W_P is the Wiener process associated with the random fluctuations of the piston. Note that when $\gamma_P = \sigma_P = 0$, the EOM shown in equation 5 reduce to the EOM corresponding to the extended system approach (i.e., a Hoover barostat) (*13*). W_ε is usually expressed as $W_\varepsilon = \left(N_f + d\right)k_\mathrm{B}T\tau_P^2$, where τ_P is the characteristic time of the barostat that should be chosen slightly larger than the smallest time scale of the particle motions (*14*). Analogous to constant-temperature DPD, the dissipative and random force parameters must conform to the FDT corresponding to the isothermal-isobaric probability density. These constraints are satisfied by imposing the constant-temperature FDT relations

$$
\begin{aligned}
\sigma_{ij}^2 &= 2\gamma_{ij}k_\mathrm{B}T \\
\omega^D\left(r\right) &= \left[\omega^R\left(r\right)\right]^2
\end{aligned}
\quad , \tag{6}
$$

along with a FDT relating the piston parameters, given as

$$
\sigma_P^2 = 2\gamma_P W_\varepsilon k_\mathrm{B}T \, , \tag{7}
$$

where k_B is the Boltzmann constant and T is the temperature. The FPE and an outline of the derivation of the FDT are presented in appendix A. With further analogy to constant-temperature DPD, the conservation of the total momentum is again due to pairwise additivity of the conservative, dissipative, and random forces. Furthermore, in the limit of $\gamma_{ij}\to 0$ and $\gamma_P \to 0$, the system conserves the quantity $E' = K + U + P_0V + \frac{p_\varepsilon^2}{2W_\varepsilon}$ where $K=\sum_i \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{2m_i}$ is the kinetic energy and $U=\sum_i\sum_{j>i}u_{ij}^{CG}$ is the configurational energy. For completeness, the EOM for nonuniform dilation is given in appendix B.

2.3 Numerical Discretization

Jakobsen (*3*) integrated the EOM given in equation 5 using a modified velocity-Verlet algorithm. In this work, we propose the numerical discretization of equation 5 using a splitting strategy similar to that employed for the constant-temperature DPD formulation presented previously, the Shardlow-splitting velocity-Verlet algorithm (SSA-VV) (*6*). The deterministic differential equations and the elementary stochastic differential equations (SDEs) corresponding to equation 5 are as follows. The conservative terms are

$$\begin{aligned} \mathrm{d}\mathbf{r}_i &= \frac{\mathbf{p}_i}{m_i}\mathrm{d}t + \frac{p_\varepsilon}{W_\varepsilon}\mathbf{r}_i\mathrm{d}t \\ \mathrm{d}\mathbf{p}_i &= \sum_{j\neq i}\mathbf{F}_{ij}^C\mathrm{d}t - \left(1+\frac{d}{N_f}\right)\frac{p_\varepsilon}{W_\varepsilon}\mathbf{p}_i\mathrm{d}t \qquad (i=1,\ldots,N)\,, \\ \mathrm{d}\ln V &= \frac{dp_\varepsilon}{W_\varepsilon}\mathrm{d}t \\ \mathrm{d}p_\varepsilon &= F_\varepsilon\mathrm{d}t \end{aligned} \tag{8}$$

while the fluctuation-dissipation terms have the same expressions as the constant-temperature DPD formulation,

$$\begin{aligned} \mathrm{d}\mathbf{p}_i^{i\text{-}j} &= -\gamma_{ij}\omega^D\left(\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\right)\frac{\mathbf{r}_{ij}}{r_{ij}}\mathrm{d}t + \sigma_{ij}\omega^R\frac{\mathbf{r}_{ij}}{r_{ij}}\mathrm{d}W_{ij} \qquad \left(\text{for each } i<j\right), \\ \mathrm{d}\mathbf{p}_j^{i\text{-}j} &= -\mathrm{d}\mathbf{p}_i^{i\text{-}j} \end{aligned} \tag{9}$$

where the superscript $i-j$ indicates that the variation of momenta is considered for a pair of interacting particles i and j only, and $\mathrm{d}W_{ij} = \mathrm{d}W_{ji}$ are the increments of the Wiener processes.

The stochastic flow map $\phi_{\Delta t}$ can be approximated by (*6*, *15*)

$$\phi_{\Delta t} \cong \phi_{\Delta t;1,2}^{diss} \circ \phi_{\Delta t;1,3}^{diss} \circ \ldots \circ \phi_{\Delta t;i,j}^{diss} \circ \ldots \circ \phi_{\Delta t;N-2,N}^{diss} \circ \phi_{\Delta t;N-1,N}^{diss} \circ \phi_{\Delta t}^{C}\,, \tag{10}$$

where $\circ$ denotes a composition of operators. For each $\phi_{\Delta t;i,j}^{diss}$ term, momenta updates are based upon the constant-temperature DPD formulation previously given (*6*):

$$\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right) = \mathbf{p}_i(t) - \frac{\Delta t}{2}\gamma_{ij}\omega^D\left[\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}(t)\right]\frac{\mathbf{r}_{ij}}{r_{ij}} + \frac{\sqrt{\Delta t}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\,, \tag{11a}$$

$$\mathbf{p}_j\left(t+\frac{\Delta t}{2}\right) = \mathbf{p}_j(t) + \frac{\Delta t}{2}\gamma_{ij}\omega^D\left[\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}(t)\right]\frac{\mathbf{r}_{ij}}{r_{ij}} - \frac{\sqrt{\Delta t}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\,, \tag{11b}$$

$$\mathbf{p}_i(t+\Delta t)=\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)-\frac{\Delta t}{2}\frac{\gamma_{ij}\omega^D}{1+\frac{\mu_{ij}}{2}\gamma_{ij}\omega^D\Delta t}\left\{\left[\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\left(t+\frac{\Delta t}{2}\right)\right]\frac{\mathbf{r}_{ij}}{r_{ij}}+\sqrt{\Delta t}\,\frac{\mu_{ij}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\right\}$$
$$+\frac{\sqrt{\Delta t}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}} \qquad (11c)$$

and

$$\mathbf{p}_j(t+\Delta t)=\mathbf{p}_j\left(t+\frac{\Delta t}{2}\right)+\frac{\Delta t}{2}\frac{\gamma_{ij}\omega^D}{1+\frac{\mu_{ij}}{2}\gamma_{ij}\omega^D\Delta t}\left\{\left[\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\left(t+\frac{\Delta t}{2}\right)\right]\frac{\mathbf{r}_{ij}}{r_{ij}}+\sqrt{\Delta t}\,\frac{\mu_{ij}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\right\}$$
$$-\frac{\sqrt{\Delta t}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}} \qquad (11d)$$

where the superscript $i-j$ has been omitted for notational simplicity, $\zeta_{ij}=\zeta_{ji}$ is a Gaussian random number with zero mean and unit variance that is chosen independently for each pair of interacting particles, and $\mu_{ij}=\frac{1}{m_i}+\frac{1}{m_j}$.

$\phi^C_{\Delta t}$ can be treated using the velocity-Verlet scheme proposed by Martyna et al. (*13*, *14*), which requires the calculation of quantities at both $t+\Delta t$ and $t+\frac{\Delta t}{2}$, followed by an iterative process to determine the remaining quantities at $t+\Delta t$. This scheme proceeds by first solving the following set of equations:

$$p_\varepsilon\left(t+\frac{\Delta t}{2}\right)=p_\varepsilon(t)+\frac{\Delta t}{2}F_\varepsilon(t)$$
$$\varepsilon(t+\Delta t)=\varepsilon(t)+\Delta t\frac{dp_\varepsilon\left(t+\frac{\Delta t}{2}\right)}{W_\varepsilon}$$
$$V(t+\Delta t)=V(0)\exp\left[\varepsilon(t+\Delta t)\right]$$
$$L(t+\Delta t)=V(t+\Delta t)^{1/3}$$
$$\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)=\mathbf{p}_i(t)+\frac{\Delta t}{2}\left[\mathbf{F}_i^C(t)-\left(2+\frac{d}{N_f}\right)\frac{p_\varepsilon(t)}{W_\varepsilon}\mathbf{p}_i(t)\right]\qquad(i=1,\ldots,N) \qquad (12a)$$
$$\mathbf{r}_i(t+\Delta t)=\exp\left[\varepsilon(t+\Delta t)-\varepsilon(t)\right]\left[\mathbf{r}_i(t)+\Delta t\frac{\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)}{m_i}\right]$$

where $L(0)$ and $L(t+\Delta t)$ are the lengths of the cubic simulation box at $t=0$ and $t+\Delta t$, respectively. Next, the conservative forces at $t+\Delta t$, $\{\mathbf{F}_i^C(t+\Delta t)\}_{i=1}^N$, are evaluated and subsequently used in the second part of the algorithm, which requires an iterative approach. The iteration starts with an estimation of p_ε at $t+\Delta t$ using $p_\varepsilon^{(0)}(t+\Delta t)=p_\varepsilon(t-\Delta t)+2\Delta t F_\varepsilon(t)$, followed by solving the set of equations

$$\mathbf{p}_i^{(k)}(t+\Delta t)=\frac{\exp\left[\varepsilon(t+\Delta t)-\varepsilon(t)\right]\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)+\frac{\Delta t}{2}\mathbf{F}_i^C(t+\Delta t)}{1+\frac{\Delta t}{2}\left(2+\frac{d}{N_f}\right)\frac{p_\varepsilon^{(k-1)}(t+\Delta t)}{W_\varepsilon}} \qquad (i=1,\ldots,N)$$

$$F_\varepsilon^{(k)}(t+\Delta t)=dV(t+\Delta t)\left[P^{(k)}(t+\Delta t)-P_0\right]+\frac{d}{N_f}\sum_i\frac{\mathbf{p}_i^{(k)}(t+\Delta t)\cdot\mathbf{p}_i^{(k)}(t+\Delta t)}{m_i} \qquad (12b)$$

$$-\gamma_P p_\varepsilon^{(k-1)}(t+\Delta t)+\sigma_P\frac{\zeta_P}{\sqrt{\Delta t}}$$

$$p_\varepsilon^{(k)}(t+\Delta t)=p_\varepsilon\left(t+\frac{\Delta t}{2}\right)+\frac{\Delta t}{2}F_\varepsilon^{(k)}(t+\Delta t)$$

self-consistently until $\left|\frac{\sum_i\left[\mathbf{p}_i^{(k)}(t+\Delta t)-\mathbf{p}_i^{(k-1)}(t+\Delta t)\right]^2}{3N}\right|$ is less than a prescribed tolerance, which is typically less than 10^{-6}. In equation (12b), ζ_P is a Gaussian random number with zero mean and unit variance and (k) is the iteration index.

The practical implementation of the SSA-VV approach for the DPD-P variant is analogous to the constant-temperature DPD formulation (*6*) with the exception that the deterministic integration steps are replaced by equations 12a and 12b. For completeness, the numerical discretization for nonuniform dilation is given in appendix B.

1. *Stochastic Integration* for all $i-j$ pairs of particles

   (i) $\mathbf{p}_i \leftarrow \mathbf{p}_i-\frac{\Delta t}{2}\gamma_{ij}\omega^D\left(\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\right)\frac{\mathbf{r}_{ij}}{r_{ij}}+\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\frac{\sqrt{\Delta t}}{2}$

   (ii) $\mathbf{p}_j \leftarrow \mathbf{p}_j+\frac{\Delta t}{2}\gamma_{ij}\omega^D\left(\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\right)\frac{\mathbf{r}_{ij}}{r_{ij}}-\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\frac{\sqrt{\Delta t}}{2}$

   (iii) $\mathbf{v}_{ij} \leftarrow \frac{\mathbf{p}_i}{m_i}-\frac{\mathbf{p}_j}{m_j}$

(iv) $\mathbf{p}_i \leftarrow \mathbf{p}_i - \frac{\Delta t}{2}\frac{\gamma_{ij}\omega^D}{1+\frac{\mu_{ij}}{2}\gamma_{ij}\omega^D\Delta t}\left[\left(\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\right)\frac{\mathbf{r}_{ij}}{r_{ij}}+\frac{\mu_{ij}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\sqrt{\Delta t}\right]+\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\frac{\sqrt{\Delta t}}{2}$

(v) $\mathbf{p}_j \leftarrow \mathbf{p}_j + \frac{\Delta t}{2}\frac{\gamma_{ij}\omega^D}{1+\frac{\mu_{ij}}{2}\gamma_{ij}\omega^D\Delta t}\left[\left(\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\right)\frac{\mathbf{r}_{ij}}{r_{ij}}+\frac{\mu_{ij}}{2}\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\sqrt{\Delta t}\right]-\sigma_{ij}\omega^R\zeta_{ij}\frac{\mathbf{r}_{ij}}{r_{ij}}\frac{\sqrt{\Delta t}}{2}$

2. *Deterministic Integration #1.1*

(i) $p_\varepsilon\left(t+\frac{\Delta t}{2}\right)=p_\varepsilon(t)+\frac{\Delta t}{2}F_\varepsilon(t)$

(ii) $\varepsilon(t+\Delta t)=\varepsilon(t)+\Delta t\frac{dp_\varepsilon\left(t+\frac{\Delta t}{2}\right)}{W_\varepsilon}$

(iii) $V(t+\Delta t)=V(0)\exp\left[\varepsilon(t+\Delta t)\right]$

(iv) $L(t+\Delta t)=V(t+\Delta t)^{1/3}$

3. *Deterministic Integration #1.2* for $i=1,\ldots,N$

(i) $\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)=\mathbf{p}_i(t)+\frac{\Delta t}{2}\left[\mathbf{F}_i^C(t)-\left(2+\frac{d}{N_f}\right)\frac{p_\varepsilon(t)}{W_\varepsilon}\mathbf{p}_i(t)\right]$

(ii) $\mathbf{r}_i(t+\Delta t)=\exp\left[\varepsilon(t+\Delta t)-\varepsilon(t)\right]\left[\mathbf{r}_i(t)+\Delta t\frac{\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)}{m_i}\right]$

4. *Conservative Force Calculation*: $\left\{\mathbf{F}_i^C\right\}_{i=1}^N$

5. *Deterministic Integration #2.1*

$$p_\varepsilon^{(0)}(t+\Delta t)=p_\varepsilon(t-\Delta t)+2\Delta t F_\varepsilon(t)$$

6. *Deterministic Integration #2.2* for $i=1,\ldots,N$

(i) $\mathbf{p}_i^{(k)}(t+\Delta t)=\frac{\exp\left[\varepsilon(t+\Delta t)-\varepsilon(t)\right]\mathbf{p}_i\left(t+\frac{\Delta t}{2}\right)+\frac{\Delta t}{2}\mathbf{F}_i^C(t+\Delta t)}{1+\frac{\Delta t}{2}\left(2+\frac{d}{N_f}\right)\frac{p_\varepsilon^{(k-1)}(t+\Delta t)}{W_\varepsilon}}$

(ii) $F_\varepsilon^{(k)}(t+\Delta t)=dV(t+\Delta t)\left[P^{(k)}(t+\Delta t)-P_0\right]+\frac{d}{N_f}\sum_i\frac{\mathbf{p}_i^{(k)}(t+\Delta t)\cdot\mathbf{p}_i^{(k)}(t+\Delta t)}{m_i}$

$$-\gamma_P p_\varepsilon^{(k-1)}(t+\Delta t)+\sigma_P\frac{\zeta_P}{\sqrt{\Delta t}}$$

7. *Deterministic Integration #2.3*

$$p_\varepsilon^{(k)}(t+\Delta t) = p_\varepsilon\left(t+\frac{\Delta t}{2}\right) + \frac{\Delta t}{2} F_\varepsilon^{(k)}(t+\Delta t)$$

Steps 6 and 7 are carried out self-consistently until $\left|\frac{\sum_i \left[\mathbf{p}_i^{(k)}(t+\Delta t) - \mathbf{p}_i^{(k-1)}(t+\Delta t)\right]^2}{3N}\right|$ is less than a prescribed tolerance.

3. Computational Details

The SSA-VV for the DPD-P method was tested using both the standard DPD fluid (*7*) and a coarse-grain solid model (*8*); complete details of the conservative forces for these models are given in appendix C. Both a pure component case and an equimolar binary mixture were tested for the DPD fluid model. System sizes for the DPD fluids and coarse-grain solid were, respectively, $N = 10125$ and 13500. For these simulations, the following reduced units were used: r_c and r_0 are the unit of length for the DPD fluid and coarse-grain solid, respectively; the mass of a DPD particle is the unit of mass; and the unit of energy is $k_\mathrm{B}T$. Using these reduced units, we set the maximum repulsion between particles i and j as $a_{ij} = 25$ for the pure DPD fluid. For the binary DPD fluid, the values were $a_{ij} = 25$ and 28 for the like and unlike $i-j$ interactions, respectively. Further, for all cases, we set the noise amplitude $\sigma_{ij} = 3$ and the barostat characteristic time $\tau_P = 2$. Prescriptions for the choice of γ_P (*3, 14*) suggest that the value should be between $2/\tau_P$ and $10/\tau_P$; therefore, we set $\gamma_P = 10/\tau_P = 5$ for all cases.

4. Results

As a test of the SSA-VV formulation, we verify that the DPD-P variant converges to the same equilibrium properties when at the same thermodynamic conditions as a constant-temperature DPD simulation.

4.1 DPD Fluid

The benchmark systems for both the pure and binary DPD fluid cases are taken from a constant-temperature DPD simulation performed at $\rho = 3$ and $T = 1$ and run for $t_{run} = 3000$ and $\Delta t = 0.03$. The following quantities were evaluated and are listed in table 1 (pure fluid) and table 2 (equimolar binary fluid): virial pressure $\langle P_{vir} \rangle$, configurational energy per particle $\langle u \rangle$, kinetic temperature $\langle T_{kin} \rangle$, and self-diffusion coefficients D using the Einstein relation (*11*).

To validate the constant-pressure SSA-VV formulations, DPD-P simulations were performed using both the Langevin and Hoover barostats with an imposed pressure determined from the constant-temperature DPD simulation ($P_0 = 23.65$ and $P_0 = 24.79$ for the pure and equimolar binary DPD fluids, respectively) for $t_{run} = 3000$ and $\Delta t = 0.03$. The results for the pure and equimolar binary DPD fluids are summarized in tables 1 and 2, respectively, where excellent agreement between the DPD-P and constant-temperature DPD simulations are found for $\langle u \rangle$, $\langle T_{kin} \rangle$, the particle density $\langle \rho \rangle = \left\langle \frac{N}{V} \right\rangle$, and D. As a further test, DPD-P simulations were also started from a random configuration subject to an energy minimization (as opposed to starting from the equilibrated configuration of the constant-temperature DPD simulation), where again calculated quantities were in excellent agreement with constant-temperature DPD results (not shown).

Table 1. The configurational energy per particle $\langle u \rangle$, the kinetic temperature $\langle T_{kin} \rangle$, the virial pressure $\langle P_{vir} \rangle$, the particle density $\langle \rho \rangle$, and the self-diffusion coefficient D, determined from simulations of the pure DPD fluid. $\langle . \rangle$ denotes an ensemble average, where numbers in parentheses are uncertainties calculated from block averages.

Variant	$\langle u \rangle$	$\langle T_{kin} \rangle$	$\langle P_{vir} \rangle$	$\langle \rho \rangle$	D
DPD $\rho = 3$	4.56(1)	1.005(8)	23.65(8)	—	0.295(13)
DPD-P Langevin $P_0 = 23.65$	4.55(1)	1.005(8)	23.59(8)	2.997(8)	0.294(14)
DPD-P Hoover $P_0 = 23.65$	4.55(1)	1.004(8)	23.61(8)	2.997(8)	0.296(19)

Table 2. The configurational energy per particle $\langle u \rangle$, the kinetic temperature $\langle T_{kin} \rangle$, the virial pressure $\langle P_{vir} \rangle$, the particle density $\langle \rho \rangle$, and the self-diffusion coefficient D, determined from simulations of the equimolar binary DPD fluid. $\langle . \rangle$ denotes an ensemble average, where numbers in parentheses are uncertainties calculated from block averages.

Variant	$\langle u \rangle$	$\langle T_{kin} \rangle$	$\langle P_{vir} \rangle$	$\langle \rho \rangle$	D_1	D_2
DPD $\rho = 3$	4.76(1)	1.005(8)	24.79(13)	—	0.177(13)	0.165(13)
DPD-P Langevin $P_0 = 24.79$	4.76(2)	1.004(8)	24.76(4)	2.998(8)	0.176(15)	0.163(17)
DPD-P Hoover $P_0 = 24.79$	4.76(1)	1.004(8)	24.75(4)	2.998(9)	0.179(12)	0.165(9)

4.2 Coarse-Grain Solid

A validation study analogous to the DPD fluids study above is performed for a coarse-grain solid model, where a recently developed nickel model is considered that reasonably reproduces several measured properties, including the melting temperature (*8*). For a benchmark system, a constant-temperature DPD simulation is performed at $\rho = 8260$ kg/m^3 and $T = 1300$ K for $t_{run} = 1$ ns and $\Delta t = 5$ fs, where results are listed in table 3. (Since the coarse-grain solid model has been parameterized to an actual material, results are reported in real units as opposed to reduced units for the DPD fluid.) At this state point, the atomistic Sutton-Chen model of nickel predicts a pressure of approximately 0 bar (*8*), while $\langle P_{vir} \rangle$ for the coarse-grain solid model is larger than 0 bar. Starting from an equilibrated configuration from a constant-temperature DPD simulation, nonuniform dilation DPD-P simulations were performed using both the Langevin and Hoover barostats at $P_0 = 0$ bar for $t_{run} = 1$ ns and $\Delta t = 5$ fs, where results are given in table 3. Compared to the constant-temperature DPD case, the DPD-P results are in near exact agreement for both barostats.

Table 3. The molar configurational energy $\langle u \rangle$, the kinetic temperature $\langle T_{kin} \rangle$, the virial pressure $\langle P_{vir} \rangle$, and the mass density $\langle \rho \rangle$, determined from simulations of the coarse-grain solid model of nickel. $\langle . \rangle$ denotes an ensemble average, where numbers in parentheses are uncertainties calculated from block averages.

Variant	$\langle u \rangle$ **(kJ/mol)**	$\langle T_{kin} \rangle$ **(K)**	$\langle P_{vir} \rangle$ **(bar)**	$\langle \rho \rangle$ **(kg/m^3)**
DPD $\rho = 8260$ kg/m^3	–508.44(11)	1300.1(91)	5.91(94)	—
DPD-P Langevin $P_0 = 0$ bar	–508.43(14)	1299.9(92)	–0.13(95)	8259.3(73)
DPD-P Hoover $P_0 = 0$ bar	–508.44(14)	1299.7(91)	0.06(99)	8260.1(68)

5. Conclusion

Comprehensive descriptions of numerical integration schemes based upon the SSA were presented for the isothermal-isobaric DPD method. The SSA was readily extendable to both the Hoover and Langevin barostats under both uniform and nonuniform dilation, where the SSA for all variants was found to be a stable and accurate integration scheme. The equivalence of the DPD variants was verified using both a standard DPD fluid model and a coarse-grain solid model, where thermodynamic quantities were considered.

6. References

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Appendix A. Fokker-Planck Equation (FPE) and Fluctuation-Dissipation Theorem (FDT)

The FPE corresponding to the equations of motion (EOM) given by equation 5 of the report is

$$\frac{\partial \rho}{\partial t} = L_C \rho + L_D \rho + L_{LB} \rho \,, \tag{A-1}$$

where the conservative operator is

$$\begin{aligned} L_C \equiv & -\left(\sum_i \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_i \sum_{j \neq i} \mathbf{F}_{ij}^C \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) - \left[\frac{p_\varepsilon}{W_\varepsilon} \sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \left(1 + \frac{d}{N_f} \right) \frac{p_\varepsilon}{W_\varepsilon} \sum_i \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] \\ & - \frac{\mathrm{d}V}{\mathrm{d}t} \frac{\partial}{\partial V} - \left[dV\left(P - P_0\right) + \frac{d}{N_f} \sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i} \right] \frac{\partial}{\partial p_\varepsilon} \end{aligned} \,. \tag{A-2}$$

The operator that accounts for the effects of the dissipative and random forces, L_D, is given by

$$L_D \equiv \sum_i \sum_{j \neq i} \frac{\mathbf{r}_{ij}}{r_{ij}} \cdot \frac{\partial}{\partial \mathbf{p}_i} \left[\gamma_{ij} \omega^D \left(\frac{\mathbf{r}_{ij}}{r_{ij}} \cdot \mathbf{v}_{ij} \right) + \frac{\sigma_{ij}^2}{2} \left(\omega^R \right)^2 \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \cdot \frac{\mathbf{r}_{ij}}{r_{ij}} \right], \tag{A-3}$$

where m_i is the mass of particle i, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the separation vector between particle i and particle j, $r_{ij} = \left| \mathbf{r}_{ij} \right|$, $\mathbf{F}_{ij}^C$ is the conservative force acting between particle i and particle j, γ_{ij} and σ_{ij} are the friction coefficient and noise amplitude between particle i and particle j, respectively, $\mathbf{v}_{ij} = \frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}$, and ω^D and ω^R are weight functions of the dissipative and random forces, respectively. The operator representing the Langevin barostat terms in the EOM is

$$L_{LB} \equiv \frac{\partial}{\partial p_\varepsilon} \left(\gamma_P p_\varepsilon + \frac{\sigma_P^2}{2} \frac{\partial}{\partial p_\varepsilon} \right). \tag{A-4}$$

In equations (A-1–A-4): $\rho \equiv \rho\left(\mathbf{r}, \mathbf{p}, V, p_\varepsilon; t\right)$, V is the system volume, p_ε is the momentum conjugate to $\varepsilon = \ln \frac{V}{V(0)}$, $V(0)$ is the volume at $t = 0$, W_ε is a mass parameter associated with ε, P is the instantaneous pressure, P_0 is the imposed pressure, d is the dimensionality of the system, $N_f = dN - d$, and γ_P and σ_P are Langevin barostat parameters.

In addition to the system's implicit contact with a heat reservoir as in the previous constant-temperature case, constant-pressure dissipative particle dynamics introduces a barostat that keeps the system pressure constant through implicit contact with a piston. Under these circumstances, the equilibrium probability density $\rho^{eq} \equiv \rho^{eq}(\mathbf{r},\mathbf{p},V,p_\varepsilon)$ then corresponds to the isothermal-isobaric probability density

$$\begin{aligned}\rho^{eq}(\mathbf{r},\mathbf{p},V,p_\varepsilon) &= \frac{1}{\Omega}\exp\left[-\frac{H(\mathbf{r},\mathbf{p})+P_0V+\frac{p_\varepsilon^2}{2W_\varepsilon}}{k_\mathrm{B}T}\right] \\ &= \frac{1}{\Omega}\exp\left(-\frac{\sum_i \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{2m_i}+\sum_i\sum_{j>i}u_{ij}^{CG}+P_0V+\frac{p_\varepsilon^2}{2W_\varepsilon}}{k_\mathrm{B}T}\right)\end{aligned}, \tag{A-5}$$

where Ω is the normalizing partition function. Similarly, as before, $L_C\rho^{eq}=0$ since the isothermal-isobaric probability density is the equilibrium solution for the conservative system. The FDT then follows from the requirements that $L_D\rho^{eq}=0$ and $L_{LB}\rho^{eq}=0$. The former leads to[1]

$$\begin{aligned}\sigma_{ij}^2 &= 2\gamma_{ij}k_\mathrm{B}T \\ \left(\omega^R\right)^2 &= \omega^D\end{aligned}, \tag{A-6}$$

while the latter is satisfied for

$$\sigma_P^2 = 2\gamma_P W_\varepsilon k_\mathrm{B}T\,. \tag{A-7}$$

Note that the temperature of the Langevin barostat corresponds to the temperature of the heat reservoir, which maintains the system temperature. Therefore, the amplitude of the volume fluctuations depends not only on the Langevin barostat parameters but also on the system temperature.

[1]Brennan, J. K.; Lísal, M. *Dissipative Particle Dynamics at Isothermal Conditions Using Shardlow-Like Splitting Algorithms*; ARL-TR-6582; U.S. Army Research Laboratory: Aberdeen Proving Ground, September 2013.

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Appendix B. Constant Pressure Dissipative Particle Dynamics (DPD-P) for Nonuniform Dilation

For constant-temperature and constant-pressure nonuniform dilation using a Langevin barostat, the equations of motion are given as

$$
\begin{aligned}
d\mathrm{r}_{\mathrm{i},\alpha} &= \frac{\mathrm{p}_{\mathrm{i},\alpha}}{\mathrm{m}_{\mathrm{i}}} d\mathrm{t} + \frac{\mathrm{p}_{\varepsilon,\alpha}}{\mathrm{W}_{\varepsilon}} \mathrm{r}_{\mathrm{i},\alpha} \mathrm{dt} \\
d\mathrm{p}_{\mathrm{i},\alpha} &= \sum_{\mathrm{j}\neq\mathrm{i}} \left(\mathrm{F}^{\mathrm{C}}_{\mathrm{ij},\alpha} + \mathrm{F}^{\mathrm{D}}_{\mathrm{ij},\alpha} + \mathrm{F}^{\mathrm{R}}_{\mathrm{ij},\alpha} \right) d\mathrm{t} - \frac{\mathrm{p}_{\varepsilon,\alpha}}{\mathrm{W}_{\varepsilon}} \mathrm{p}_{\mathrm{i},\alpha} d\mathrm{t} \\
&\quad - \frac{\mathrm{p}_{\varepsilon,\mathrm{x}} + \mathrm{p}_{\varepsilon,\mathrm{y}} + \mathrm{p}_{\varepsilon,\mathrm{z}}}{3\mathrm{N}_{\mathrm{f}} \mathrm{W}_{\varepsilon}} \mathrm{p}_{\mathrm{i},\alpha} d\mathrm{t} \qquad (\mathrm{i} = 1,..., \mathrm{N}) \,, \qquad \text{(B-1)} \\
d \ln \mathrm{L}_{\alpha} &= \frac{\mathrm{p}_{\varepsilon,\alpha}}{\mathrm{W}_{\varepsilon}} d\mathrm{t} \\
d\mathrm{p}_{\varepsilon,\alpha} &= \mathrm{F}_{\varepsilon,\alpha} d\mathrm{t}
\end{aligned}
$$

where: $\alpha \equiv (x, y, z)$, $\varepsilon_\alpha = \ln \frac{L_\alpha}{L_\alpha(0)}$, L_α and $L_\alpha(0)$ are the box lengths for the α-direction at t and $t = 0$, respectively, $p_{\varepsilon,\alpha}$ is the momentum conjugate to ε_α, W_ε is the mass parameter associated with ε_α, typically set to $W_\varepsilon = \frac{1}{3}(N_f + 3) k_\mathrm{B} T \tau_P^2$, τ_P is the barostat characteristic time, $N_f = 3N - 3$, $F_{\varepsilon,\alpha} = V(P_{\alpha\alpha} - P_0) + \frac{1}{N_f} \sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i} - \gamma_P p_{\varepsilon,\alpha} + \sigma_P W_{p,\alpha}$,

$P_{\alpha\beta} = \frac{1}{V} \left(\sum_i \frac{p_{i,\alpha} p_{i,\beta}}{m_i} + \sum_i \sum_{j>i} F^C_{ij,\alpha} r_{ij,\beta} \right)$ is the component of the pressure tensor for the α and β directions, P_0 is the imposed pressure, $V = L_x L_y L_z$, γ_P and σ_P are the Langevin barostat parameters, $\sigma_P^2 = 2\gamma_P W_\varepsilon k_\mathrm{B} T$ is the FDT relating the piston parameters, and $W_{P,\alpha}$ is the Wiener process associated with the random fluctuations of the piston in the α-direction.

B.1 Numerical Discretization

Applying a numerical integration splitting strategy similar to the uniform dilation DPD-P variant, the deterministic differential equations and the elementary stochastic differential equations (SDEs) corresponding to equation B-1 are as follows. The conservative terms are

$$
\begin{aligned}
\mathrm{d}r_{i,\alpha} &= \frac{p_{i,\alpha}}{m_i} \mathrm{d}t + \frac{p_{\varepsilon,\alpha}}{W_\varepsilon} r_{i,\alpha} \mathrm{d}t \\
\mathrm{d}p_{i,\alpha} &= \sum_{j\neq i} F^C_{ij,\alpha} \mathrm{d}t - \frac{p_{\varepsilon,\alpha}}{W_\varepsilon} p_{i,\alpha} \mathrm{d}t - \frac{p_{\varepsilon,x} + p_{\varepsilon,y} + p_{\varepsilon,z}}{3N_f W_\varepsilon} p_{i,\alpha} \mathrm{d}t \qquad (i = 1,..., N) \,, \qquad \text{(B-2)} \\
\mathrm{d} \ln L_\alpha &= \frac{p_{\varepsilon,\alpha}}{W_\varepsilon} \mathrm{d}t \\
\mathrm{d}p_{\varepsilon,\alpha} &= F_{\varepsilon,\alpha} \mathrm{d}t
\end{aligned}
$$

while the fluctuation-dissipation terms consist of the elementary SDEs:

$$\begin{aligned} \mathrm{d}\mathbf{p}_{i}^{i\text{-}j} &= -\gamma_{ij}\omega^{D}\left(\frac{\mathbf{r}_{ij}}{r_{ij}}\cdot\mathbf{v}_{ij}\right)\frac{\mathbf{r}_{ij}}{r_{ij}}\mathrm{d}t + \sigma_{ij}\omega^{R}\frac{\mathbf{r}_{ij}}{r_{ij}}\mathrm{d}W_{ij} \\ \mathrm{d}\mathbf{p}_{j}^{i\text{-}j} &= -\mathrm{d}\mathbf{p}_{i}^{i\text{-}j} \end{aligned} \qquad \left(\text{for each } i<j\right). \qquad \text{(B-3)}$$

As previously stated, the stochastic flow map $\phi_{\Delta t}$ is approximated by equation 10 of the report. For each fluctuation-dissipation term $\phi_{\Delta t;i,j}^{diss}$, momenta are updated by applying the same expressions as in the uniform dilation case, i.e., equations 11a, 11b, 11c, and 11d of the report. $\phi_{\Delta t}^{C}$ can be treated using the velocity-Verlet scheme proposed by Martyna et al.,[1,2] which requires the calculation of quantities at both $t+\Delta t$ and $t+\frac{\Delta t}{2}$, followed by an iterative process to determine the remaining quantities at $t+\Delta t$. This scheme proceeds by first solving the following set of equations

$$\begin{aligned} p_{\varepsilon,\alpha}\left(t+\frac{\Delta t}{2}\right) &= p_{\varepsilon,\alpha}(t)+\frac{\Delta t}{2}F_{\varepsilon,\alpha}(t) \\ \varepsilon_{\alpha}(t+\Delta t) &= \varepsilon_{\alpha}(t)+\Delta t\frac{p_{\varepsilon,\alpha}\left(t+\frac{\Delta t}{2}\right)}{W_{\varepsilon}} \\ L_{\alpha}(t+\Delta t) &= L_{\alpha}(0)\exp\left[\varepsilon_{\alpha}(t+\Delta t)\right] \\ V(t+\Delta t) &= L_{x}(t+\Delta t)L_{y}(t+\Delta t)L_{z}(t+\Delta t) \\ p_{i,\alpha}\left(t+\frac{\Delta t}{2}\right) &= p_{i,\alpha}(t)+\frac{\Delta t}{2}\left[F_{i,\alpha}^{C}(t)-2\frac{p_{\varepsilon,\alpha}(t)}{W_{\varepsilon}}p_{i,\alpha}(t)-\frac{p_{\varepsilon,x}(t)+p_{\varepsilon,y}(t)+p_{\varepsilon,z}(t)}{3N_{f}W_{\varepsilon}}p_{i,\alpha}(t)\right] \quad (i=1,\ldots,N) \\ r_{i,\alpha}(t+\Delta t) &= \exp\left[\varepsilon_{\alpha}(t+\Delta t)-\varepsilon_{\alpha}(t)\right]\left[r_{i,\alpha}(t)+\Delta t\frac{p_{i,\alpha}\left(t+\frac{\Delta t}{2}\right)}{m_{i}}\right] \end{aligned} \qquad \text{. (B-4a)}$$

Next, the conservative forces at $t+\Delta t$, $\left\{\mathbf{F}_{i}^{C}(t+\Delta t)\right\}_{i=1}^{N}$, are evaluated and subsequently used in the second part of the algorithm, which requires iteration. The iteration process starts with an estimation of $p_{\varepsilon,\alpha}$ at $t+\Delta t$ using $p_{\varepsilon,\alpha}^{(0)}(t+\Delta t)=p_{\varepsilon,\alpha}(t-\Delta t)+2\Delta t F_{\varepsilon,\alpha}(t)$, followed by solving the set of equations

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[1] Martyna, G. J.; Tobias, D. J.; Klein, M. L. Constant Pressure Molecular Dynamics Algorithms. *J. Chem. Phys.* **1994**, *101*, 4177.

[2] Martyna, G. J.; Tuckerman, M. E.; Tobias, D. J.; Klein, M. L. Explicit Reversible Integrators for Extended Systems Dynamics. *Mol. Phys.* **1996**, *87*, 1117–1157.

$$p_{i,\alpha}^{(k)}(t+\Delta t)=\frac{\exp\left[\varepsilon_\alpha(t+\Delta t)-\varepsilon_\alpha(t)\right]p_{i,\alpha}\left(t+\frac{\Delta t}{2}\right)+\frac{\Delta t}{2}F_{i,\alpha}^{C}(t+\Delta t)}{1+\frac{\Delta t}{2}\left[2\frac{p_{\varepsilon,\alpha}^{(k-1)}(t+\Delta t)}{W_\varepsilon}+\frac{p_{\varepsilon,x}^{(k-1)}(t+\Delta t)+p_{\varepsilon,y}^{(k-1)}(t+\Delta t)+p_{\varepsilon,z}^{(k-1)}(t+\Delta t)}{3N_f W_\varepsilon}\right]}\quad (i=1,\ldots,N)$$

$$F_{\varepsilon,\alpha}^{(k)}(t+\Delta t)=V(t+\Delta t)\left[P_{\alpha\alpha}^{(k)}(t+\Delta t)-P_0\right]+\frac{1}{N_f}\sum_i\frac{\mathbf{p}_i^{(k)}(t+\Delta t)\cdot\mathbf{p}_i^{(k)}(t+\Delta t)}{m_i} \qquad \text{(B-4b)}$$

$$-\gamma_P p_{\varepsilon,\alpha}^{(k-1)}(t+\Delta t)+\sigma_P\frac{\varsigma_{P,\alpha}}{\sqrt{\Delta t}}$$

$$p_{\varepsilon,\alpha}^{(k)}(t+\Delta t)=p_{\varepsilon,\alpha}\left(t+\frac{\Delta t}{2}\right)+\frac{\Delta t}{2}F_{\varepsilon,\alpha}^{(k)}(t+\Delta t)$$

self-consistently until $\left|\frac{\sum_i\left[\mathbf{p}_i^{(k)}(t+\Delta t)-\mathbf{p}_i^{(k-1)}(t+\Delta t)\right]^2}{3N}\right|$ is less than a prescribed tolerance, which is typically chosen to be $O(10^{-6})$. In equation (B-4b), $\varsigma_{P,\alpha}$ is a Gaussian random number with zero mean and unit variance and (k) is the iteration index.

Appendix C. Simulation Model Details

For the models considered in this work, the details of the conservative forces expressed in equation 2 of the main text are the following. u_{ij}^{CG} for the pure and binary Dissipative Particle Dynamics (DPD) fluids[1] is given by

$$u_{ij}^{CG} = a_{ij} r_c \omega^D\left(r_{ij}\right), \tag{C-1}$$

where a_{ij} is the maximum repulsion between particle i and particle j.

For the coarse-grain solid model, which has a face-centered-cubic (f.c.c.) lattice structure, particles interact through a shifted-force Sutton-Chen embedded potential (SC) given as

$$\mathrm{u_i^{CG}} = \varepsilon\left(\frac{1}{2}\sum_{\mathrm{j\neq i}} \mathrm{u_{ij}^{rep}} - \mathrm{c}\sqrt{\rho_i}\right), \tag{C-2}$$

where

$$\mathrm{u_{ij}^{rep}} = \mathrm{v}\left(\mathrm{r_{ij}}\right) - \mathrm{v}\left(\mathrm{r_{ij}} = \mathrm{r_c}\right) - \frac{\mathrm{dv}\left(\mathrm{r_{ij}}\right)}{\mathrm{dr_{ij}}}|_{\mathrm{r_{ij}}=\mathrm{r_c}}\left(\mathrm{r_{ij}} - \mathrm{r_c}\right),$$

$$\mathrm{v}\left(\mathrm{r_{ij}}\right) = \left(\frac{\mathrm{r_0}}{\mathrm{r_{ij}}}\right)^{\mathrm{n}},$$

$$\rho_i = \sum_{\mathrm{j\neq i}} \rho_{ij},$$

$$\rho_{ij} = \mathrm{w}\left(\mathrm{r_{ij}}\right) - \mathrm{w}\left(\mathrm{r_{ij}} = \mathrm{r_c}\right) - \frac{\mathrm{dw}\left(\mathrm{r_{ij}}\right)}{\mathrm{dr_{ij}}}|_{\mathrm{r_{ij}}=\mathrm{r_c}}\left(\mathrm{r_{ij}} - \mathrm{r_c}\right),$$

$$\mathrm{w}\left(\mathrm{r_{ij}}\right) = \left(\frac{\mathrm{r_0}}{\mathrm{r_{ij}}}\right)^{\mathrm{m}},$$

[1] Groot, R. D.; Warren, P. B. Dissipative Particle Dynamics: Bridging the Gap Between Atomistic and Mesoscopic Simulation. *J. Chem. Phys*. **1997**, *107*, 4423.

where ε and r_0 are the energy and length parameters, respectively, n and m are positive integers ($n > m$ to satisfy elastic stability of the crystal), and c is a dimensionless parameter. Although effectively this is a many-body potential, the force on each particle can be written as a sum of pairwise contributions. The coarse-grain solid model used here approximates nickel (Ni), where one DPD particle was chosen to represent four f.c.c. unit cells, i.e., 16 Ni atoms. SC potential parameters were determined by fitting to various 0-K properties and the melting temperature at zero pressure,[2] where the following values were found: $\varepsilon / k_{\mathrm{B}} = 225\,\mathrm{K}$, $r_0 = 8.8698$ Å, $c = 39.4314$, $m = 6$, and $n = 9$. Further details for determining SC parameters based upon such a procedure can be found elsewhere.[2,3]

[2]Brennan, J. K.; Lísal, M. Coarse-Grain Models for Metals: Constant-Pressure Dissipative Dynamics Simulations. In *Proceedings of the 14th International Detonation Symposium*, Coeur d'Alene, ID,11–16 April 2010; Office of Naval Research, 2010; p 1451.

[3]Sutton, A. P.; Chen, J. Long-Range Finnis-Sinclair Potentials. *J. Philos. Mag. Lett.* **1990**, *61* (3), 139.

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List of Symbols, Abbreviations, and Acronyms

DPD	constant-temperature Dissipative Particle Dynamics
DPD-P	constant-temperature, constant-pressure Dissipative Particle Dynamics
EOM	equations of motion
f.c.c.	face-centered-cubic
FDT	fluctuation-dissipation theorem
FPE	Fokker-Planck equation
SC	Sutton-Chen embedded potential
SDE	stochastic differential equation
SSA	Shardlow-splitting algorithm
SSA-VV	Shardlow-splitting algorithm-velocity Verlet

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